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Title:

Solid oxide **fuel cells** of ceria doped with gadolinium and praseodymium

Authors:

Maffei, N.^a; Kuriakose, A.K.^a

Affiliations:

a. Materials Technology Laboratories, CANMET, Natural Resources Canada, 405
Rochester St., Ottawa, Canada K1A 0G3

Address:

(No address specified)

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N. Maffei*, A.K. Kuriakose

Materials Technology Laboratories, CANMET, Natural Resources Canada, 405 Rochester St., Ottawa, Canada K1A 0G3

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Abstract

Planar solid oxide fuel cells (SOFC) incorporating a single ceria electrolyte element, doubly doped with gadolinium and praseodymium were fabricated, and tested at 700°C. Two fuel cell configurations were investigated, platinum/ceria/platinum and platinum/ceria/perovskite. Argon–4% hydrogen was used at the anode and air at the cathode. The J – V and power density characteristics of these cells are reported; it appears that the doubly doped ceria also possesses considerable electronic conductivity. Thermogravimetric analysis of the electrolyte in hydrogen shows a chemical reduction of the material beginning at about 700°C.

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PACS: 84.60.-h; 84.60.Dn; 84.60.Bk

1. Introduction

Fuel cells are relatively benign, highly efficient devices that convert chemical energy directly into electrical energy [1–3]. By far, the most widely studied and most developed solid oxide fuel cell (SOFC) is based on ZrO_2 electrolyte, which exhibits purely ionic conductivity at 1000°C. However, the high operating temperature of this cell places stringent requirements on the construction materials that can be used in these devices. Lowering the operating temperature would increase the reliability and operating life of the fuel cell. Consequently, materials

such as stainless steel could be used which would simplify the overall cell design.

Ceria-based electrolytes show an ionic conductivity at 700°C similar to ZrO_2 at 1000°C [4,5], but unfortunately, these electrolytes are not pure ionic conductors; they are plagued by electronic conductivity which is detrimental to their fuel cell operation. In addition, the electrolyte is not stable under the hydrogen environment found at the anode.

Attempts have been made to reduce the electronic conductivity by doping the ceria with ions such as gadolinium and samarium [5–7] without success, and recently, a double doping scheme has been proposed which would reduce electronic conductivity and increase stability under hydrogen atmospheres [8]. The purpose of this work is to synthesize and characterize samples of the proposed doubly doped

*Corresponding author. Tel: (613) 992-1391; fax: (613) 992-9389; e-mail: nmaffei@NRCan.gc.ca

ceria, and to test the performance aspects of a planar type SOFC incorporating the same electrolyte. The results are presented in this paper.

2. Experimental

The doubly doped ceria electrolyte ($\sim \text{Ce}_{0.8}\text{Gd}_{0.10}\text{Pr}_{0.01}\text{O}_{1.905}$) was prepared by conventional ceramic processing techniques [9]. High purity oxides (CeO_2 , Gd_2O_3 , and Pr_6O_{11} , all 99.99%, purchased from Alfa Aesar) were ground and then attrition milled in isopropyl alcohol for 1 h. The dried powder was subsequently calcined at 1000°C in air for 8 h, to get the oxides reacted. Samples 3.175 cm in diameter and 1–2 mm nominal thickness were prepared by mixing the calcined powder with a 15% PVA solution and uniaxially pressing it at 69 MPa, resulting in a green density of greater than 50%. The samples were then isostatically pressed at 275 MPa, which increased the green density to 60–65%. The pellets were sintered at 1600°C for 12 h in air with a heating and cooling rate of 5°C min^{-1} . The sintered density of all the samples was greater than 97% of the expected theoretical value.

Conductivity of the ceria electrolyte was determined by impedance measurements made with an HP4192A LF impedance analyzer. The frequency range investigated was 0.01–1000 kHz, with an oscillator level of 50 mV. The spectra were analyzed with a Boukamp fitting program [10,11]. Engelhard platinum paste A-3380 was applied to both sides of the ceria discs which were then fired at 1000°C for 1 h in air. The conductivity data were collected under a compressed air flow of $100 \text{ cm}^3 \text{ min}^{-1}$.

TG/DTA studies to determine the stability of the ceria electrolyte in a hydrogen atmosphere were conducted and the evolved gases were analyzed with a Bomem MB100 FTIR spectrometer. Pieces of sintered samples weighing 15 mg were used for these experiments. Runs were made in platinum pans at a heating rate of $20^\circ\text{C min}^{-1}$ to 1000°C in a $100 \text{ cm}^3 \text{ min}^{-1}$ gas purge.

Two planar single cell configurations were fabricated for fuel cell evaluation; one structure utilized Engelhard platinum ink A-4338 for both the anode and cathode electrodes. The electrodes were air dried and then fired at 1000°C for 1 h in air, with heating

and cooling rates of $10^\circ\text{C min}^{-1}$. The other cell configuration studied used the same platinum ink for the anode but a perovskite, $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LCFC) for the cathode. The preparation of the perovskite has been previously described [12,13]. The calcined oxide powder was ground and mixed with a polyvinyl butyral binder, ethanol, and a polyethylene glycol plasticizer, as described in [12,14]. The slurry was brushed onto the ceria substrate and sintered at 1150°C for 5 h with heating and cooling rates of 5°C min^{-1} . During fuel cell operation, a 4% H_2 /96% Ar gas mixture at a flow of $10 \text{ cm}^3 \text{ min}^{-1}$ was supplied at the anode while a flow of compressed air at $50 \text{ cm}^3 \text{ min}^{-1}$ was maintained at the cathode. Platinum mesh was placed on top of the anode and cathode to act as current collectors.

3. Results and discussion

Impedance spectroscopy was used to determine the total conductivity (bulk plus intergranular) of the doped ceria electrolyte. The high temperature spectra ($T > 600^\circ\text{C}$) revealed the presence of an inductance, on the order of 2 microhenri, for high frequencies, above approximately 50 kHz. The inductance was, however, easily subtracted from the spectra by a Boukamp fitting program [10,11].

The total conductivity (σT) versus reciprocal temperature is given in Fig. 1. The data exhibited an Arrhenius type behaviour of the form:

$$\sigma T = \sigma_0 \exp(E/kT)$$

where E is activation energy, k Boltzmann's constant and T absolute temperature. The activation energy obtained from a NLLS fit of the data was $(0.7 \pm 0.05) \text{ eV}$, in good agreement with previously reported values [4,15,16].

A major concern with ceria based electrolytes is their stability under the reducing hydrogen environment present at the anode. Fig. 2 shows the result of TG studies done in pure He and in 4% H_2 -He gas mixture. After heating to 1000°C in helium, the ceria electrolyte showed no weight change, the slight weight loss and subsequent gain shown in the figure being within the error margin of the instrument. No

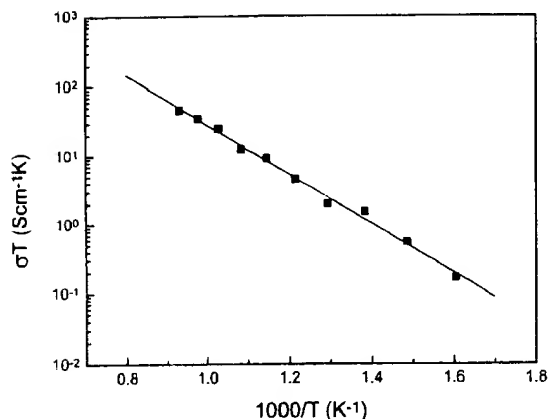


Fig. 1. Conductivity (σT) versus reciprocal temperature for a Gd-Pr doped ceria electrolyte with platinum electrodes.

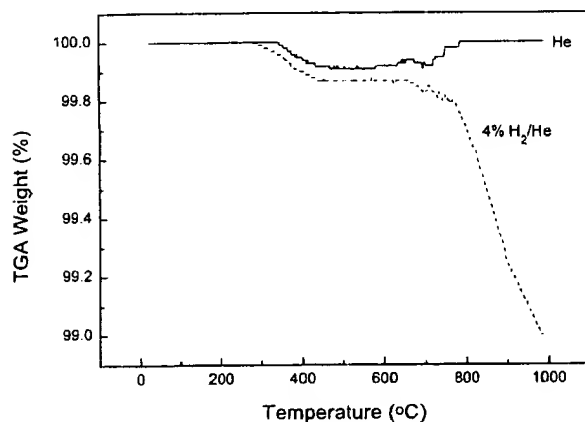


Fig. 2. TG data for Gd-Pr doped ceria electrolyte in He and 4% H_2 -He gas mixture to 1000°C, at a heating rate of 20°C min⁻¹.

evolved gases, other than background, were detected by FTIR.

A sample heated in 4% H_2 -He started to lose weight at around 700°C, and the weight loss rate became rapid around 800°C. This weight loss was accompanied by H_2O evolution, as detected by FTIR, in the same temperature range, indicating the chemical reduction of the doped ceria electrolyte. This reduced sample turned dark grey after heating, while the sample heated in pure helium did not change colour. These data suggest that a fuel cell incorporating the doubly doped ceria electrolyte may be safely operated at around 700°C for long periods of time; but at temperatures approaching 800°C, the device will be unstable. The data also suggest that

the double doping scheme was not entirely effective in preventing the reduction of the ceria electrolyte in hydrogen.

The J - V characteristics of a planar SOFC incorporating a single 1.09 mm thick ceria disc with porous platinum electrodes are shown in Fig. 3. The cell was operated continuously for 120 h without showing any signs of deterioration; rather, as indicated in the figure, the cell performance improved with time. The linear J - V data indicate that the potential drop of the device was mostly due to the IR drop across the electrolyte. The lower than expected cell voltage [8,17] can be attributed to the presence of significant electronic conductivity. The power density for the same fuel cell is shown in Fig. 4. The relatively low values for current and power densities

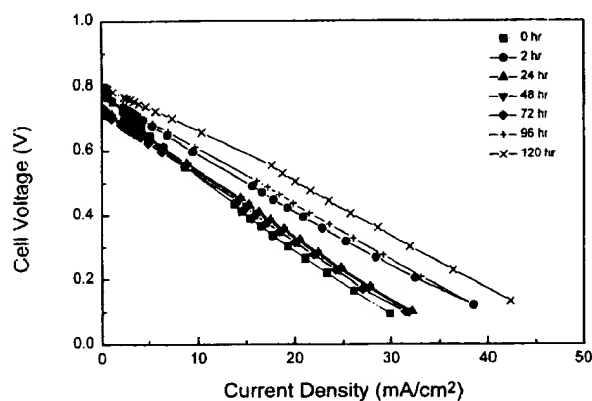


Fig. 3. J - V data for a single planar fuel cell with the Pt/ceria/Pt configuration.

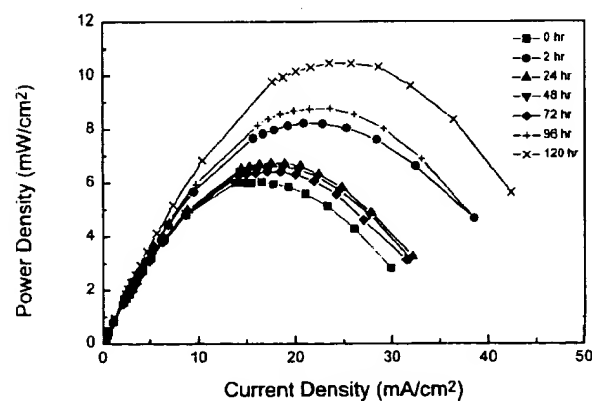


Fig. 4. Power density versus current density plot for the fuel cell referred to in Fig. 3.

can also be ascribed to the presence of electronic conductivity [15] and to the large thickness of the ceria electrolyte [16]. In spite of these factors, the ceria based SOFC performed satisfactorily in agreement with previous findings [18]. The same cell was thermally cycled several times without any deterioration in performance.

No evidence of reduction of the ceria electrolyte was indicated by the J - V data. However, this does not preclude the reduction of the ceria electrolyte surface, since the TG data showed the initiation of a very slow reduction at approximately 700°C. In fact, the circumference of the ceria disc did appear darker in colour after the fuel cell trials. The degree of reduction, however, in the present setup, may have been negligible because of the large thickness of the ceria electrolyte used. A fuel cell incorporating a thin ceria electrolyte membrane may not be the same.

The high cost of platinum is a disadvantage for its use in commercial fuel cells. In addition, the oxidizing conditions present at the cathode tend to deteriorate the platinum electrode after long periods of fuel cell operation. An inexpensive alternative for the cathode is LCFC with a perovskite structure. This material has been shown to have good surface exchange coefficients and exchange current densities [19]. The J - V characteristics for a planar type fuel cell with a single 1.11 mm thick ceria disc in the Pt/ceria/perovskite configuration is shown in Fig. 5, and the corresponding power density data are presented in Fig. 6. Again, the lower than expected cell voltage indicates the presence of significant elec-

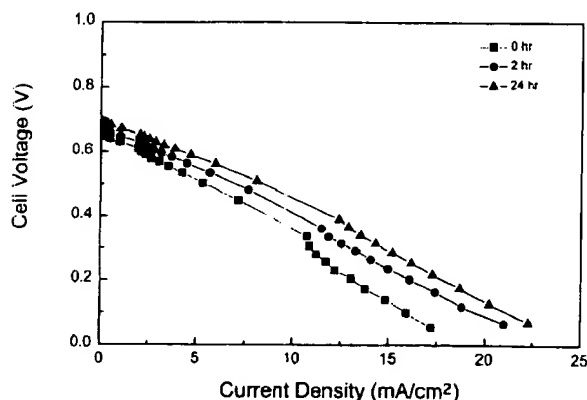


Fig. 5. J - V data for a single planar fuel cell with a LCFC perovskite cathode and a platinum anode.

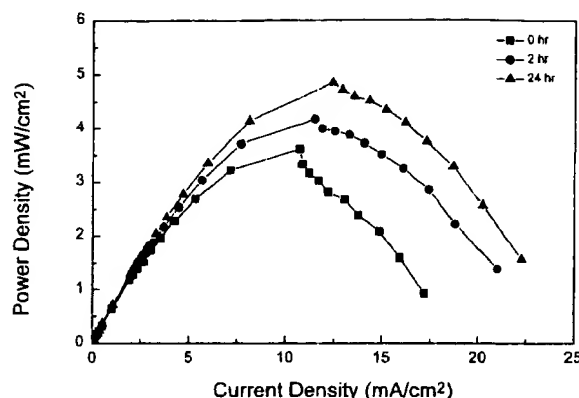


Fig. 6. Power density characteristics for the fuel cell referred to in Fig. 5.

tronic conduction. Although, the overall characteristics of this cell are similar to the Pt/ceria/Pt based fuel cell, the performance was inferior. Even after 24 h of operation the power density of this cell was less than the initial power density levels of the Pt cathode cell. Clearly, the LCFC/ceria electrolyte interface was not performing as well as the Pt/ceria counterpart. This suggests that the LCFC electrode and/or its thickness needs to be further optimized. The cell was thermally cycled several times and again did not show any deterioration of the device.

The double doping scheme proposed by Maricle et al. [8] was claimed to significantly lower the electrolyte domain boundary, defined as the oxygen partial pressure ($p_{\text{O}_2} \sim 10^{-21}$ atm) at which the ionic conductivity became equal to the electronic conductivity [9]. Steele et al. [20], however, did not measure any appreciable difference in p_{O_2} for singly or doubly doped ceria electrolyte, at least for temperatures $\leq 800^\circ\text{C}$. The presence of significant electronic conductivity in the present fuel cell, as revealed by the J - V data, are consistent with the data presented by Steele et al. [20]. Given these data, the use of doubly doped ceria electrolyte in SOFC, as opposed to singly doped ceria, does not seem to offer any benefits.

4. Summary

Doubly doped ceria electrolyte was fabricated and incorporated into a planar SOFC and tested at 700°C.

The J – V data for two different cathode electrode configurations indicated the presence of significant electronic conductivity in the electrolyte. These data suggest that the double doping scheme was not effective in reducing the electronic conduction present in the ceria electrolyte. Thermogravimetric analysis of the electrolyte in hydrogen showed a chemical reduction of the oxide by hydrogen beginning at around 700°C. Nevertheless, the fuel cells were stable over relatively long periods, and did not show any signs of deterioration even after several thermal cycles. The performance of a fuel cell with a perovskite cathode was inferior to one incorporating a platinum cathode. This indicated that the cathode/ceria electrolyte interface need to be further optimized to increase the performance of the cell.

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